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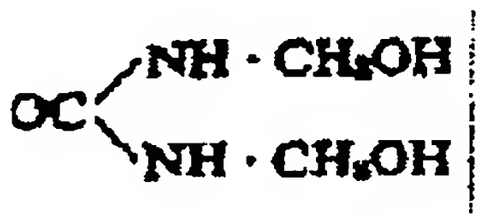
Chemical preservatives

It is known that formaldehyde in the form of ether-like compounds with alcohol, such as, for example, as an acetal or hemiacetal, can be bound as a depot substance, which then eliminates free formaldehyde monomer. The germicidal action of formaldehyde is therefore also afforded by the use of such acetals and hemiacetals. It has been shown that the hemiacetals, in particular, for example the semiformals of poly-alcohols, such as ethylene glycol, 1,2-propylene glycol, triethylene glycol or alternatively butyl triglycol, can be employed as bactericidally and bacteriostatically active agents. The decomposition rate of such acetals and hemiacetals of formaldehyde is very different and accordingly the time of preservation is variable within a wide period.

Such glycol formals or glycol polyformals have been used for the production of non-iron textiles, the elimination of formaldehyde likewise being of importance because of the chemical binding to the cellulose fibres. Such acetals and hemiacetals of formaldehyde have proved very effective for industrial preservation, since they develop a wide bactericidal action against bacteria, fungi, yeasts and a number of spore-forming agents. The elimination of formaldehyde in general takes place particularly easily in the acidic range. It has been shown that the bactericidal and bacteriostatic action does not last for an unlimited length of time, particularly in stirred systems, such as, for example, with cooling liquids in the metal industry, but is slowly used up, be it as a result of consumption by microorganisms or by evaporation of the formaldehyde.

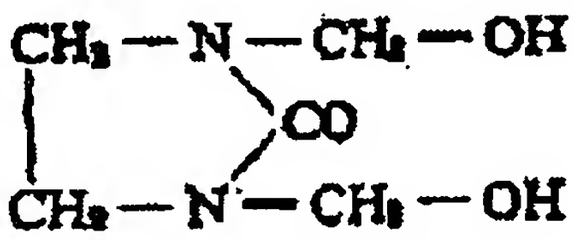
It has now been found that as a result of the combination of such acetals with a number of methylol compounds a considerable advance in industrial preservation is achieved. For instance, the acetals or hemiacetals of ethylene glycol or 1,2-propylene glycol were combined with formaldehyde-eliminating nitrogen-methylol products, such as dimethylolurea, dimethylol-ethyleneurea and similar substances. Dimethylolurea [Formula (I)] and the other complementary components possess a mainly bacteriostatic action as, because of their stability, they only slowly become active with elimination of formaldehyde in the course of many days and weeks.



(I)

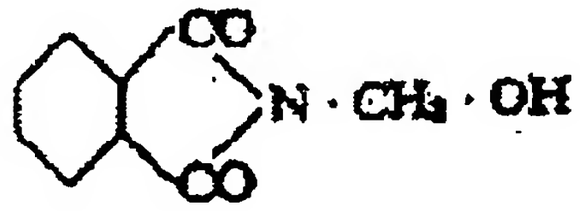
The cleavage tendency is not only dependent on certain medium conditions such as the pH, but to a great extent on the chemical structure of these compounds. While the formals eliminate formaldehyde relatively easily and are thus particularly bactericidalally mobilizable in their preserving action, as a result of the presence of relatively stable compounds, such as dimethylolurea, an industrially particularly convenient interaction is achieved, which significantly prolongs and also increases the bacteriostatic and bactericidal activity of the entire combined mechanism in terms of time. By means of the acetal, a premature pantropic formalin action with great microorganism reduction is achieved, which particularly favourably influences the mainly bacteriostatic action of the nitrogen-methylol compounds. In addition, there is the fact that both types of chemical preservatives apparently mutually complement each other in such a way that on consumption of the one component the other partly reforms it again.

These combinations are especially also very highly active in a neutral or alkaline-reacting medium. The dimethylol compound of ethyleneurea (Formula II),



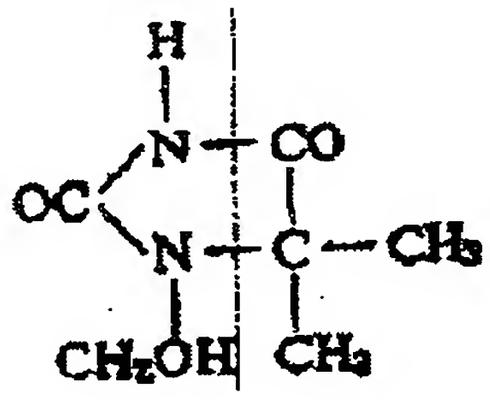
(II)

furthermore the monomethylol compound of phthalimide



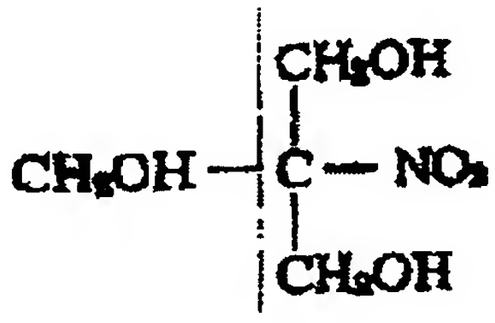
(III)

and its derivatives, and 1-methylol-5,5'-dimethyl hydantoin (Formula IV)



(IV)

also act similarly to dimethylolurea. The use of tris-hydroxymethylnitromethane (Formula V)



(V)

in combination with the acetals described has proved advantageous. The compound is already known per se as a bactericide.

The bacteriostatically and bactericidalally active preservatives described are suitable as an addition to

liquid and pasty raw materials and finished preparations which are endangered by attack by microorganisms. Thus they can be used, for example, for adhesives, raw materials and cosmetic finished preparations, cooling agents in the metal industry, and for the impregnation of paper and non-wovens, for example based on cellulose.

Example 1

Preservative, consisting of
70 parts of ethylene glycol acetal and
30 parts of dimethylolurea.

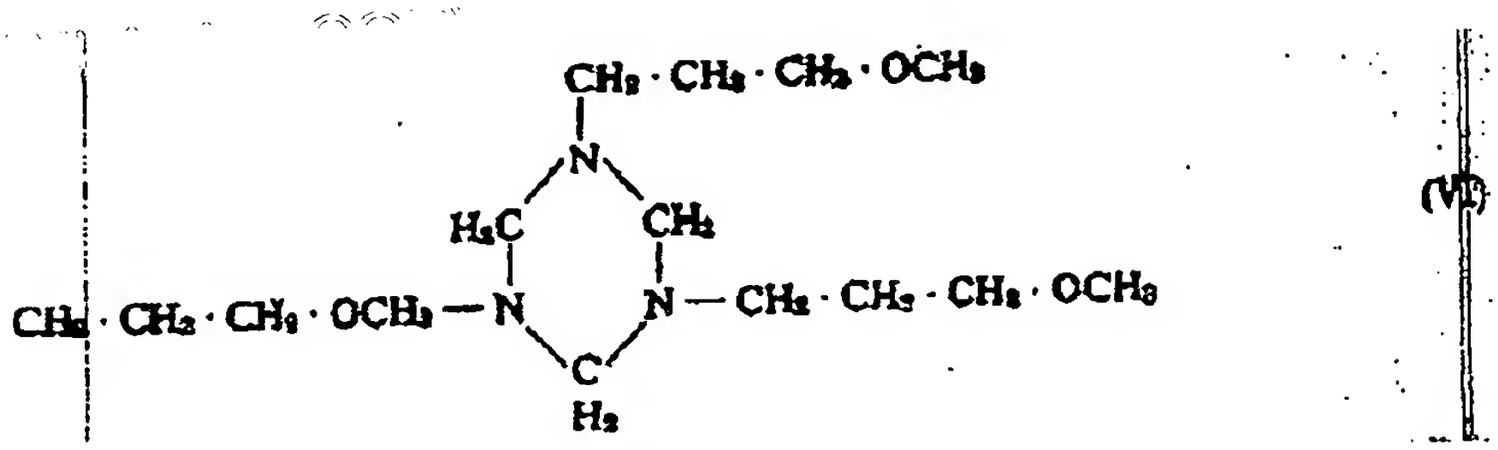
Example 2

Preservative, consisting of
20 parts of dimethylolethyleneurea and
80 parts of glycol acetal.

Example 3

Preservative, consisting of
35 parts of 1,2-propylene glycol acetal,
15 parts of dimethylolurea and
15 parts of substituted hexahydrotriazine compound.

Re a more detailed explanation of the hexahydrotriazine compound: Here, for example, the condensation product of 1 mol of methoxypropylamine with 1 mol of paraformaldehyde is to be used (Formula VI)



(VI)

In order to achieve particular bactericidal effects, within the meaning of Example 3 the mixture of acetals with nitrogen-methylol compounds can also be combined with other disinfectants, e.g. from the group consisting of the aminoacetals. The combination of the acetal-containing compounds with the nitrogen-methylol compounds has the advantage of covering a wide range in the spectrum of the microorganisms. In terms of application technology, they are especially characterized by their good water solubility. However, incorporation into lipid systems is also easily possible by the addition of solubilizers for covering a mixing gap.

Because of the good preserving action, the amount of the addition can be kept so low that the toxic action on the skin either of formaldehyde or of the nitrogen-methylol compounds cannot occur. Practical skin tests have also shown that the feared sensitization in the form of contact allergies both on the part of the nitrogen compounds and on the part of the acetals only extends to a very small group of people. In addition to wide activity, this crucial advantage makes these preservatives particularly utilizable for use in preparations which lead to heavy skin contact on account of their intended use. For instance, hair shampoos, face lotions or face creams have a long-lasting contact with the skin to a greater or lesser extent. The customary preservatives, such as, for example, mercury compounds, phenols, sorbic acid or oxybenzoic acid are then either too harmful to the skin or have to be employed in a concentration which

crucially changes the character of the cosmetic preparations. Because of its volatility, formaldehyde has only a short-lasting action; compounds containing free chlorine are not utilizable because of the skin intolerability and the lability of active chlorine. The combinations described complement each other to give a suitable combination of bactericidal and bacteriostatic effects.

With respect to drilling and cutting oils, it has been shown, particularly in the case of working operations with frequent skin contact, that the selection of a skin-tolerable and nevertheless active preservative causes extreme difficulties. The combinations described with their good properties fill the gap which exists here.

Patent claims:

1. Preservatives for liquid and pasty preparations based on condensation product of formaldehyde with primary and secondary mono- and polyalcohols, characterized in that, for achieving a wide and long-lasting activity, these are combined with nitrogen-methylol compounds.

2. Combination preparations according to Claim 1, characterized in that, as methylol-containing nitrogen compounds monomethylol-, dimethylol- or dimethylol-ethyleneureas are mainly used because of a particularly good skin tolerability.

3. Preservatives according to Claims 1 and 2, characterized by the preferable use for the preservation of oil-containing or oil-free cooling agents in metal machining.

4. Preservatives according to Claims 1 and 2, characterized by the preferable use for the preservation of raw materials and finished preparations in cosmetics.

5. Preservatives according to Claims 1 and 2, characterized in that they are combined with heterocyclic bactericides from the group consisting of the aminoacetals, for example derivatives of hexahydrotriazine or of oxazolidine.

Three tables with test results have been displayed in the publication of the application.